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**Surface Composition of Fluorinated Poly(amide urethane) Block
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Abstract: The surface composition and near surface depth profiles of solution-cast films of poly(amide urethane) block copolymers were measured using angle-dependent electron spectroscopy for chemical analysis (ESCA). Segregation of fluorinated polyamide soft segment to the surface was detected and quantified. The poly(amide urethane)s were made from amine-terminated polyamides with N-alkylated fluorinated side chains as well as fluorinated backbones, methylenebis(cyclohexane diisocyanate) ($H_{12}MDI$), and butanediol.¹ The resulting copolymers display extremely low surface energy. Annealing of the solution-cast films drives the fluorinated side chains to the surface. A deconvolution program was utilized to obtain composition depth profiles and to confirm phase segregation.

Introduction

The synthesis and characterization of low surface energy poly(amide urethane) block copolymers has been previously reported by the University of Pittsburgh group.¹ Analysis of contact angle measurements indicated a surface dominated by the fluorinated components; we are interested in further discerning the composition and morphology of the surface at the air-polymer interface. In the present work, angle-dependent electron spectroscopy for chemical analysis (ESCA) is employed, and the topmost 100Å of annealed films has been examined.

Since photoelectron intensities detected by ESCA are convoluted signals, i.e. all atoms in the path of the X-ray contribute to the signal,² deconvolution methods must be used to obtain composition depth profiles. Such methods have been employed by several research groups, including a method of regularization by Ratner et al.³ used to analyze polymers. Fulghum et al. introduced and compared different deconvolution algorithms for the determination of overlayer thicknesses and/or concentration gradients.⁴ The present work utilizes a recently developed numerical method that simulates depth profiles of the individual components in a block copolymer by introducing boundary conditions based on the composition.⁵

The series of fluorinated polyamides and their corresponding poly(amide urethane) block copolymers described in Scheme 1 and 2, were studied. Since fluorocarbons display very low surface energy,

these poly(amide urethane)s would be expected to have a low energy surface if there was microphase separation. Previous work reported contact angle measurements and determined critical surface tensions as low as 11 dyne/cm;¹ therefore, such phase segregation was suspected. The low energy surface properties of these copolymers make them potential candidates for minimal fouling coating applications.^{6,7}

Experimental

Sample Preparation:

The preparation of the poly(amide urethane) block copolymers has been previously described.¹ The structures of the copolymers and their code names are given in Schemes 1 and 2.

The films of the polymers were prepared by casting 0.2-2.0% solutions from 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), or the mixed solvents of dimethylacetamide and tetrahydrofuran onto aluminum foil. The films were annealed in an Abderhalden pistol for 48-72 hours at several degrees above their glass transition temperatures.¹ Ultrasonic extraction of the films in hexane did not produce significant differences in ESCA measurements. Thus, evanescent surface impurities can be eliminated as a contribution to the results.

Instrumentation:

Angle-dependent ESCA data were obtained using a Physical Electronics (PHI) model 5100 spectrometer equipped with a Mg/Ti dual anode source and an Al/Be window. The system uses a hemispherical analyzer with a single channel detector. Mg K α X-rays (1253.6 eV) were used as an achromatic source, operated at 300 W (15 kV and 20 mA). The base pressure of the system was lower than 5×10^{-9} torr, with an operating pressure no higher than 1×10^{-7} torr. A pass energy of 89.45 eV was used when obtaining the survey spectra, and of 35.75 eV was used for the high resolution spectra of elemental regions. Spectra were obtained at the following take-off angles: 10°, 15°, 30° and 90°. The instrument was calibrated using Mg K α X-radiation such that the distance between Au 4f_{7/2} and Au 4f_{5/2} was 3.65 eV, and the distance between Au 4f_{7/2} and Cu 2p_{3/2} was set at 848.67 eV, and the work function was set using Au 4f_{7/2}, Cu 2p_{3/2}, and checking using Au 3d_{5/2}. All metals were sputter cleaned to remove oxides. Full width at half maximum for Ag 3d_{3/2} was measured to be 0.8 eV at a count rate of 30,000 counts.

ESCA Data Calculations:

With the sensitivity factors provided in the software supplied by PHI and verified by Vargo and Gardella⁸ using polymer standards, the peak area integration and subsequent composition calculation (atomic percentages) were performed using a Perkin-Elmer 7500 professional computer running PHI ESCA Version 2.0 software. From

the atomic percentages, composition depth profiles were achieved using the following protocol.

In the previous work using the numerical method^{5,9} the poly(dimethylsiloxane urethane) (PDMS-PU) segmented copolymer chains are divided into soft and hard segments. Since nitrogen is unique to the hard segments, the weight percentage of PDMS (soft segment) or polyurethane (hard segment) can be calculated from the atomic ratio of nitrogen to carbon (N/C).⁵ In the present work, the poly(amide urethane) copolymers can be similarly divided into soft and hard blocks. However, it could be misleading to use fluorine to represent the entire soft block in the copolymer with long fluorinated side chains. For example, in copolymer 15F-6F-HB much of the fluorine is contained in the side chain. Therefore, we determined the concentration depth profile using CF_x (representing CF_2 and CF_3) segments instead.

The principle of revealing the concentration depth profile of CF_x is the same as described in Ref. 5, but the mathematical equation used to fit the experimental data is different. A five-parameter equation was introduced:

$$\begin{aligned} y(x) &= 1 - H \exp[-0.5(x-X)^2/S_1^2] (1-C) \quad x \leq X \\ &= 1 - \{b + (H-b) \exp[-0.5(x-X)^2/S_2^2]\} (1-C) \quad x > X \end{aligned}$$

where y is the volume fraction of CF_x segments, H is a parameter relevant to the magnitude of the trough on the profile, x is the distance from the surface (in Angstroms), X is the location of the

trough of the profile, S_1 characterizes the shape of the profile to the left of the trough, S_2 characterizes the shape of the profile to the right of the trough, C is the volume fraction of CF_x segments in the bulk, b evaluates the height of the plateau in the profile. Accordingly, the following objective function was used to optimize the values of those parameters.

$$\Psi = \{1/n \sum [[R_{\text{cal}}(H, X, S_1, S_2, b) - R_{\text{exp}}(\theta_n)] / R_{\text{exp}}(\theta_n)]^2 \}^{1/2}$$

where n is the number of take-off angles.

Upon data fitting, the influence of the different inelastic mean free paths (IMFP) for C_{1s} and F_{1s} electrons was considered and corrected. The IMFP for C_{1s} and F_{1s} were calculated with the modified Bethe¹⁰ equation since the Seah-Dench¹¹ equation tends to overestimate the IMFP in the low-energy region, while underestimating the IMFP in the high-energy region.¹⁰ The resultant IMFPs of C_{1s} electrons are 30Å for copolymers 0F-6F-HB, 5F-6F-HB and 5F-8F-HB (see Scheme 1 for chemical structures) with estimated densities¹² of 1.14, 1.27 and 1.22 g/cm³, respectively, and 28Å for copolymer 15F-6F-HB with an estimated density of 1.29 g/cm³. The IMFPs of F_{1s} electrons are 20Å for copolymers 0F-6F-HB, 5F-6F-HB and 5F-8F-HB, and 18Å for copolymer 15F-6F-HB.

Results and Discussion

In ESCA analysis, there are two ways to evaluate the composition in the near surface region, i.e., elemental analysis and curve-fitting.¹³ In this case, one could use either elemental

analysis of fluorine, which can be quantitatively related to the soft block, and/or the analysis of the intensity of the chemical shift due to the CF_x fraction of functional groups containing carbon.¹³ For the latter approach, a typical ESCA C_{1s} spectrum for copolymer 15F-6F-HB at 10° take-off angle is shown in Figure 1a. The large peak at $\sim 290.5 \pm 0.1$ eV represents fluorocarbons; the small middle peak represents carbonyl carbons; and the peak at $\sim 285.0 \pm 0.1$ eV identifies the hydrocarbons. The dominance of C_{1s} peak at $\sim 290.5 \pm 0.1$ eV indicates a large concentration of fluorinated polyamide soft block at the surface. In comparison with Figure 1a, the C_{1s} spectrum for copolymer 15F-6F-HB at 90° take-off angle is shown in Figure 1b, in which the amount of hydrocarbon has grown relative to fluorocarbon. It suggests that the concentration of fluorinated polyamide soft block at 10° take-off angle is higher than that at 90° . In other words, the information from C_{1s} region does show a trend of the concentration gradient of fluorinated polyamide soft blocks in the surface region. However, quantitative analysis using curve-fitting is not convenient because the inexact knowledge of binding energies of functional groups with fluorine and oxygen present makes curve-fitting in the C_{1s} region difficult.¹⁴

Alternatively, atomic percentages of fluorine (F%) were obtained from elemental analysis of ESCA results. Table 1 lists the F%'s for polyamides 0F-6F, 5F-6F, 5F-8F and 15F-6F (see Scheme 1 for chemical structures), and those for poly(amide urethane)s 0F-

6F-HB, 5F-6F-HB, 5F-8F-HB and 15F-6F-HB at four take-off angles.

Interestingly, the F%'s for polyamides in Table 1 and Figure 2 are slightly, but consistently, lower than the calculated bulk or average values. We expected that the values would be equivalent to bulk values since no phase separation is expected in these samples. As discussed previously, the IMFP for F_{1s} electrons is smaller than not only that for C_{1s} electrons, but also those for O_{1s} and N_{1s} electrons. Consequently, in the calculation of atomic percentages at a particular angle the signal intensity from F will be underestimated, on the other hand, the signal intensities for C, O and N will be relatively overestimated, thereby resulting in lower surface F%'s for polyamides than the theoretical bulk F%'s. This serves well as direct experimental evidence prompting us to factor the IMFP in the later depth profile calculations.

Of the two components in poly(amide urethane)s, the fluorinated polyamide (soft block) has a lower surface energy than the polyurethane (hard block). Thus, we expect this soft block to segregate at the air-polymer interface. The ESCA results in Table 1 and Figure 3 support this model. Even though they were under-evaluated due to the shorter IMFP of F_{1s} electrons, the measured F%'s were still significantly (95% confidence level) higher than the bulk F%'s at four take-off angles for all the poly(amide urethane)s, and the F%'s for the poly(amide urethane)s decrease from the air-polymer interface to the bulk, consistent with the

conclusion drawn from the comparison of Figures 1a and 1b. In addition, the F%'s at four take-off angles listed in Table 1 for the poly(amide urethane)s are close to those for the corresponding polyamides. This similarity suggests that there is a phase segregation so that the polyamide is coating the poly(amide urethane) block.

The extent of surface segregation of the fluorinated component strongly depends on the structure of the fluorinated poly(amide urethane)s and the bulk composition. As shown in Figure 3, copolymer 5F-6F-HB yielded a higher surface F% than 0F-6F-HB as a result of a higher percentage of the fluorinated component in the bulk and fluorinated side chain (see Scheme 2 for structure information). Copolymer 5F-8F-HB displayed a substantially higher surface F% than copolymer 5F-6F-HB although the latter has a higher bulk F% than the former. This observation could be attributed to "bending" toward the surface of the longer fluorinated segments in the backbone of copolymer 5F-8F-HB. It is of particular interest to compare copolymer 5F-6F-HB with copolymer 15F-6F-HB. Copolymer 15F-6F-HB displayed a remarkably higher F% than copolymer 5F-6F-HB even though they have almost the same bulk F%. As illustrated in Scheme 2, there are long fluorinated side chains in copolymer 15F-6F-HB. When the poly(amide urethane)s were solution-cast into a film, it is expected that the low surface energy fluorinated moieties would migrate and perhaps orient toward

surface on solvent evaporation, forming a surface morphology depicted in (or schematically illustrated) in Scheme 3.¹ Therefore, the longer the fluorinated side chain, the higher the surface F% expected.

As it is, in ESCA measurements, photoelectron intensities detected are convoluted signals, i.e., all atoms within the path of the probing X-ray contribute to the signal but the contribution of each decreases exponentially with the distance from the free surface.² The convoluted nature of the angle-dependent measurements distorts depth profiles for samples with compositional gradients. To recover the true depth profiles for such samples from atomic percentages of carbon and fluorine listed in Table 2, the modified deconvolution method, described above, was utilized.⁵

In contrast to the angle-dependent ESCA data in Table 1, which merely suggest a monotonic increase of the hard block, or a monotonic decrease of the fluorinated polyamide (soft block), from the surface to the bulk, Figure 4 displays the recovered in-depth concentration profiles for copolymers 0F-6F-HB, 5F-6F-HB, 5F-8F-HB and 15F-6F-HB. These results show segregation or surface excess regions of the soft block in the topmost layer followed immediately by the depletion regions. This latter feature of the concentration depth profile can not be measured directly with existing techniques. A reasonable explanation for this feature is that the composition of the soft block integrated over one polymer chain

length must equal its bulk composition (a constraint in our calculations). Therefore, any surface excess layer of the soft block must necessarily be followed by a depletion layer and vice versa.

Firstly, from these profiles an extrapolated "surface composition" ($x=0$) can be determined and compared. Volume fractions (v_{CF_x}) of CF_x segments at the very top surface ($x=0$) for copolymers 15F-6F-HB, 5F-8F-HB and 5F-6F-HB are 0.998, 0.919 and 0.847, respectively, while that for copolymer 0F-6F-HB is 0.461. This follows the same trend as the 10° ESCA data in Figure 3.

Secondly, as two important factors characterizing the depletion zone (the trough), the depth from the surface (i.e. the thickness of the surface excess layer) and the magnitude (y value) can be evaluated. The depths of the depletion regions for copolymers 15F-6F-HB, 5F-8F-HB, 5F-6F-HB and 0F-6F-HB are 26\AA , 29\AA , 17\AA and 12\AA from the surface. As discussed earlier, poly(amide urethane)s with long fluorinated side chains favor forming a thicker fluorine-rich layer in the surface region upon solvent evaporation when solution-cast into films. However, copolymer 0F-6F-HB does not have such luxury, and a thinner fluorine-rich topmost layer was observed. The magnitudes of the trough in the profiles for copolymers 15F-6F-HB, 5F-8F-HB and 5F-6F-HB are 0.740, 0.688 and 0.708, respectively, while that for copolymer 0F-6F-HB is 0.238. These values, 0.740, 0.688, 0.708, and 0.238, roughly correlated

with the bulk F%'s, 23.69, 16.59, 24.07 and 13.26, of the copolymers.

The other specific comparisons can be made with these data. Among the poly(amide urethane)s with fluorinated side chains, copolymers 5F-8F-HB and 5F-6F-HB have the same fluorinated side chain, but their backbones differ, as shown in Scheme 2. As a result, copolymer 5F-8F-HB gives rise to a higher surface concentration of CF_x segments ($v_{\text{CPX}}=0.919$). Furthermore, the trough of the depletion region for copolymer 5F-8F-HB locates at 29\AA while that for copolymer 5F-6F-HB locates at 17\AA . This indicates the existence of a much thicker fluorine-rich layer in the surface region of copolymer 5F-8F-HB, due to the more readily "bending" of the fluorinated backbone in copolymer 5F-8F-HB toward the surface.

Copolymers 15F-6F-HB and 5F-6F-HB have the same backbone, but, the length of their fluorinated side chains is different. As shown in Figure 5, copolymer 15F-6F-HB exhibits a significantly higher surface concentration of CF_x segments ($v_{\text{CPX}}=0.998$) and a much thicker fluorine-rich layer (26\AA) in the surface region, although it has almost the same bulk F% as copolymer 5F-6F-HB.

Although copolymer 15F-6F-HB gives rise to higher surface concentration of CF_x segments, $v_{\text{CPX}}=0.998$ ($x=0$), than copolymer 5F-8F-HB, the thickness of the fluorine-rich surface layer for the former (26\AA) is equivalent (within error limits) to that for the latter (29\AA). This puzzling observation may be attributed to the

"bending" of the fluorinated backbone in copolymer 5F-8F-HB toward the surface, further thickening the fluorine-rich surface layer.

Conclusions

The surface compositions of fluorinated polyamides and poly(amide urethane)s were studied by angle-dependent ESCA. Surface segregation was observed for poly(amide urethane) block copolymers. Higher concentrations of surface segregation were discerned for those poly(amide urethane)s with fluorinated side chains.

The composition depth profiles extracted via a numerical deconvolution method further demonstrated the phase separation of the hard and soft blocks in the copolymer. They demonstrate that poly(amide urethane)s with fluorinated side chains form higher surface concentrations of CF_x segments and thicker fluorine-rich surface layers. The molecular structures of the poly(amide urethane)s with fluorinated side chains have a profound influence on the composition depth profiles.

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References

- 1) Chapman, T. M. and Marra, K. G. *Macromolecules*, **1995**, 28, 2081-2085. See also Chapman, T. M.; Marra, K. G.; Benrashid, R. and Keener, J. P. *Macromolecules*, **1995**, 28, 331-336.
- 2) Clark, D. T. *Advances in Polymer Sciences*, **1977**, 24, 126.
- 3) Tyler, B. J.; Castner, D. G. and Ratner, B. D. *Surf. Interface Anal.* **1989**, 14, 443.
- 4) Tielsch, B. J. and Fulghum, J. E. *Surf. and Interface Anal.* **1994**, 21, 621-630.
- 5) Ho, T.; Chen, X.; Gardella, J. A. Jr. and Wynne, K. J. *Macromolecules*, **1995**, 28, 1635-1642.
- 6) Brady, R. F.; Griffith, J. R.; Love, K. S. and Field, D. E. *J. Coat. Technol.* **1987**, 59 (755), 133.
- 7) Ho, T. and Wynne, K. J. *Macromolecules*, **1992**, 25, 3521.
- 8) Vargo, T. G. and Gardella, J. A. Jr. *J. Vac. Sci. Technol.* **1989**, A7(3), May/Jun, 1733-1741.
- 9) Ho, T.; Wynne, K. J.; Gardella, J. A. Jr. and Zhuang, H. *J. Colloid Interface Sci.* in press.
- 10) Tanuma, S.; Powell, C. J. and Pen, D. *Surf. and Interface Anal.* **1993**, 21, 165-176.
- 11) Seah, M. P. and Dench, W. A. *Surf. and Interface Anal.* **1979**, 1(1), 2-11.
- 12) Brandrup, J. and Immergut, E. H. *Polymer Handbook*, Third Edition, John Wiley & Sons, 1989.

13) Schmidt, J. J.; Gardella, J. A. Jr. and Salvati, L. Jr.
Macromolecules, **1989**, 22, 4489.

14) Vargo, T. G. and Gardella, J. A. Jr. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, 29(4), 555-570.

Table 1. Atomic percentage of fluorine in the polymers ($\pm 5\%$), determined by angle-dependent ESCA, as reflected by peak ratios prior to de-convolution.

Polymer	Take-off Angle				Theoretical %F
	10°	15°	30°	90°	
0F-6F	25 ± 1.3	25 ± 1.3	20 ± 1.0	21 ± 1.1	30.14
5F-6F	49 ± 2.5	49 ± 2.5	43 ± 2.2	43 ± 2.2	53.50
5F-8F	41 ± 2.1	42 ± 2.1	39 ± 2.0	40 ± 2.0	55.31
15F-6F	57 ± 2.9	55 ± 2.8	43 ± 2.2	44 ± 2.2	64.03
0F-6F-HB	24 ± 1.2	21 ± 1.1	18 ± 0.9	16 ± 0.8	13.26
5F-6F-HB	39 ± 2.0	36 ± 1.8	32 ± 1.3	27 ± 1.4	24.07
5F-8F-HB	45 ± 2.3	44 ± 2.2	42 ± 1.4	38 ± 1.7	16.59
15F-6F-HB	52 ± 2.6	51 ± 2.6	49 ± 2.5	43 ± 2.1	23.69

**Table 2. Atomic percentage of carbon, oxygen, and nitrogen
in the poly(amide urethane) ($\pm 5\%$), prior to de-convolution.**

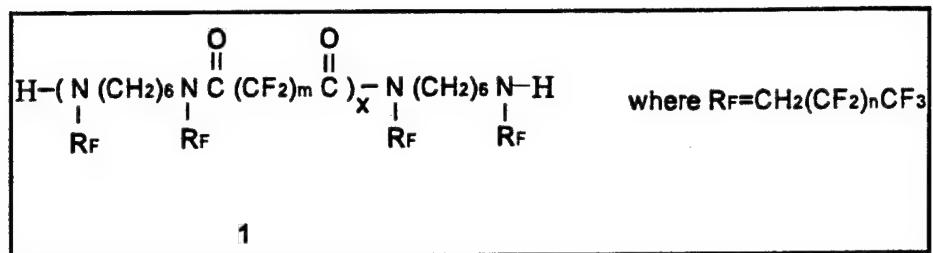
Polymer		Take-off Angle				Theoretical
		10°	15°	30°	90°	
0F-6F-HB	%C	58 ± 2.9	58 ± 2.9	56 ± 2.8	52 ± 2.6	63.68
	%O	11 ± 0.55	13 ± 0.65	18 ± 0.9	25 ± 1.3	14.91
	%N	7 ± 0.35	7 ± 0.35	8 ± 0.4	7 ± 0.35	8.15
	%F	24 ± 1.2	22 ± 1.1	18 ± 0.9	16 ± 0.8	13.26
5F-6F-HB	% C	44 ± 2.2	44 ± 2.2	41 ± 2.1	36 ± 1.8	55.38
	%O	13 ± 0.7	15 ± 0.8	22 ± 1.1	33 ± 1.6	13.52
	%N	4 ± 0.2	5 ± 0.25	5 ± 0.25	4 ± 0.2	7.03
	% F	39 ± 2.0	36 ± 1.8	32 ± 1.3	27 ± 1.4	24.07
5F-8F-HB	%C	44 ± 2.2	45 ± 2.3	47 ± 2.4	50 ± 2.5	60.40
	%O	5 ± 0.25	5 ± 0.25	5 ± 0.25	7 ± 0.35	15.53
	%N	6 ± 0.3	6 ± 0.3	6 ± 0.3	5 ± 0.25	7.48
	% F	45 ± 2.3	44 ± 2.2	42 ± 1.4	38 ± 1.7	16.59
15F-6F-HB	%C	39 ± 0.2	43 ± 2.2	43 ± 2.2	48 ± 2.4	56.14
	%O	5 ± 0.25	4 ± 0.2	5 ± 0.25	5 ± 0.25	13.69
	%N	4 ± 0.2	2 ± 0.1	3 ± 0.15	4 ± 0.2	6.48
	%F	52 ± 2.6	51 ± 2.6	49 ± 2.5	43 ± 2.1	23.69

List of Schemes

Scheme 1: Polyamide structure and code names. a: Prepared with a non-fluorinated propyl side-chain.

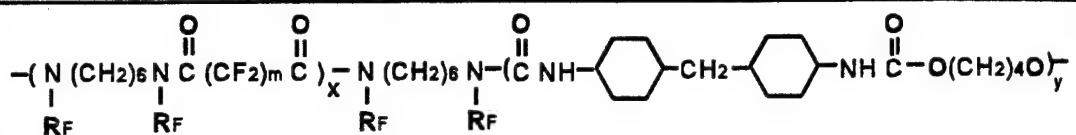
Scheme 2: Poly(amide urethane) structure and code names. H=H₁₂MDI and B=butanediol.
a: Prepared with a non-fluorinated propyl side-chain.

Scheme 3: Proposed surface structure of the poly(amide urethane)s.



	Total # Fluorines			
	n	m	per repeat unit	Code name
1a	a	3	0	0F-6F
1b	1	3	5	5F-6F
1c	1	4	5	5F-8F
1d	6	3	15	15F-6F

Scheme 1. Polyamide structure and code names. a: Prepared with a non-fluorinated propyl side-chain.



where $\text{RF} = \text{CH}_2(\text{CF}_2)_n\text{CF}_3$

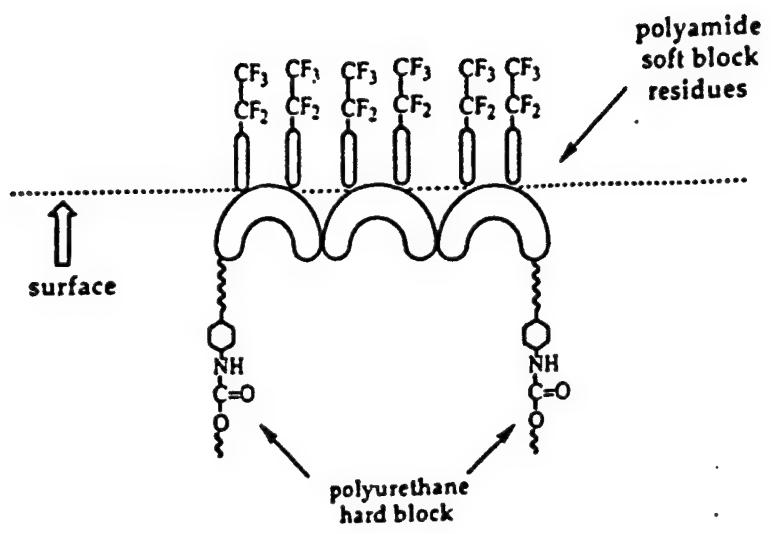
Total # Fluorines

n	m	per repeat unit of polyamide blocks	Code name	Wt.% Polyamide ¹
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2a	a	3	0	0F-6F-HB	44
2b	1	3	5	5F-6F-HB	45
2c	1	4	5	5F-8F-HB	30
2d	6	3	15	15F-6F-HB	37

Scheme 2. Poly(amide urethane) structure and code names. H=H₁₂MDI and B=butanediol.

a: Prepared with non-fluorinated propyl side-chain.



Scheme 3.

List of Figures

Figure 1a: ESCA spectrum of copolymer 15F-6F-HB in the C_{1S} region recorded at 10° take-off angle.

Figure 1b: ESCA spectrum of copolymer 15F-6F-HB in the C_{1S} region recorded at 90° take-off angle.

Figure 2: Atomic percentages of fluorine for polyamides, data taken at 10°.

Figure 3: Atomic percentages of fluorine for poly(amide urethane)s, data taken at 10°.

Figure 4: Concentration depth profiles for poly(amide urethane)s.

Fig. 12

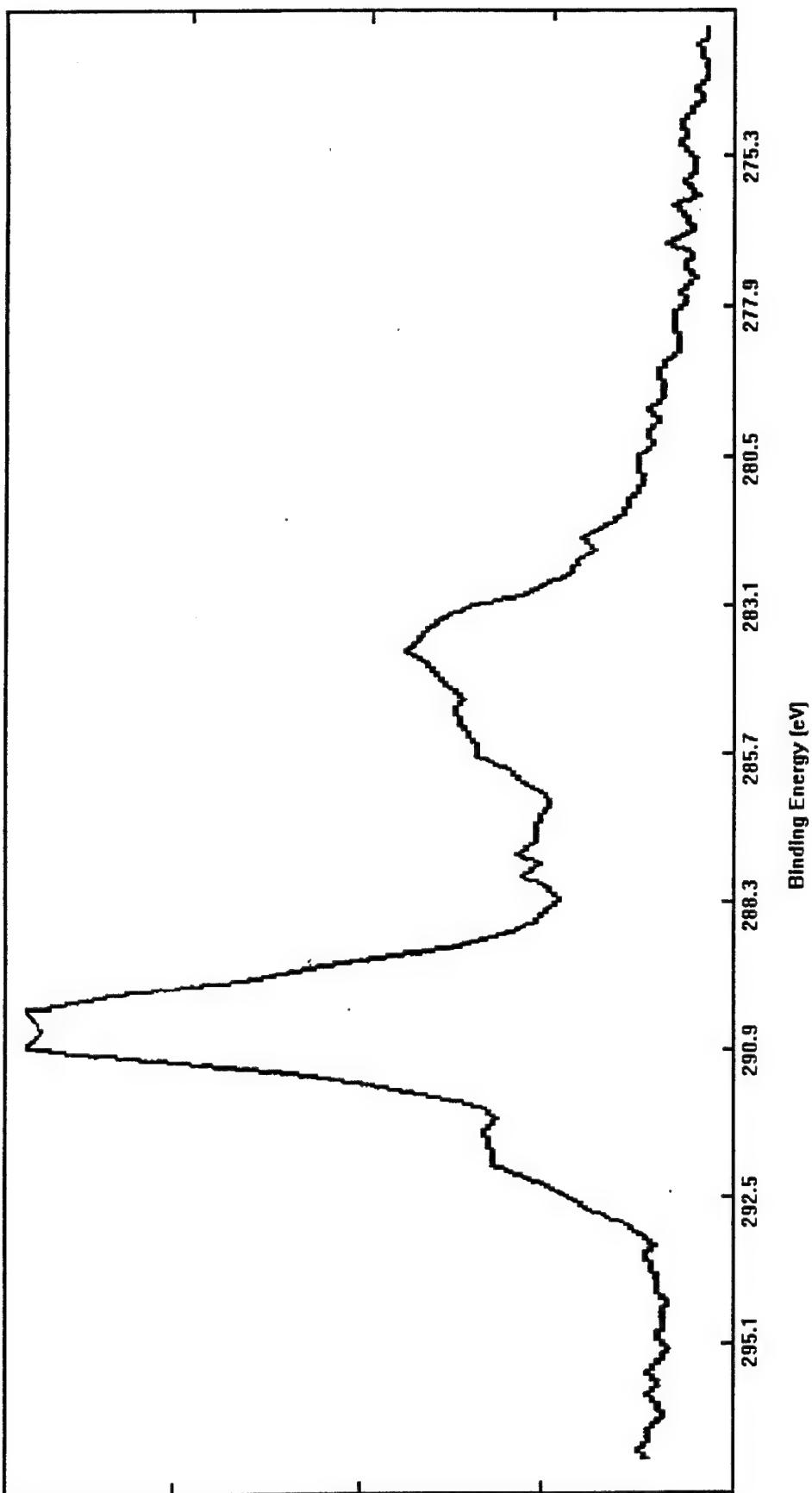
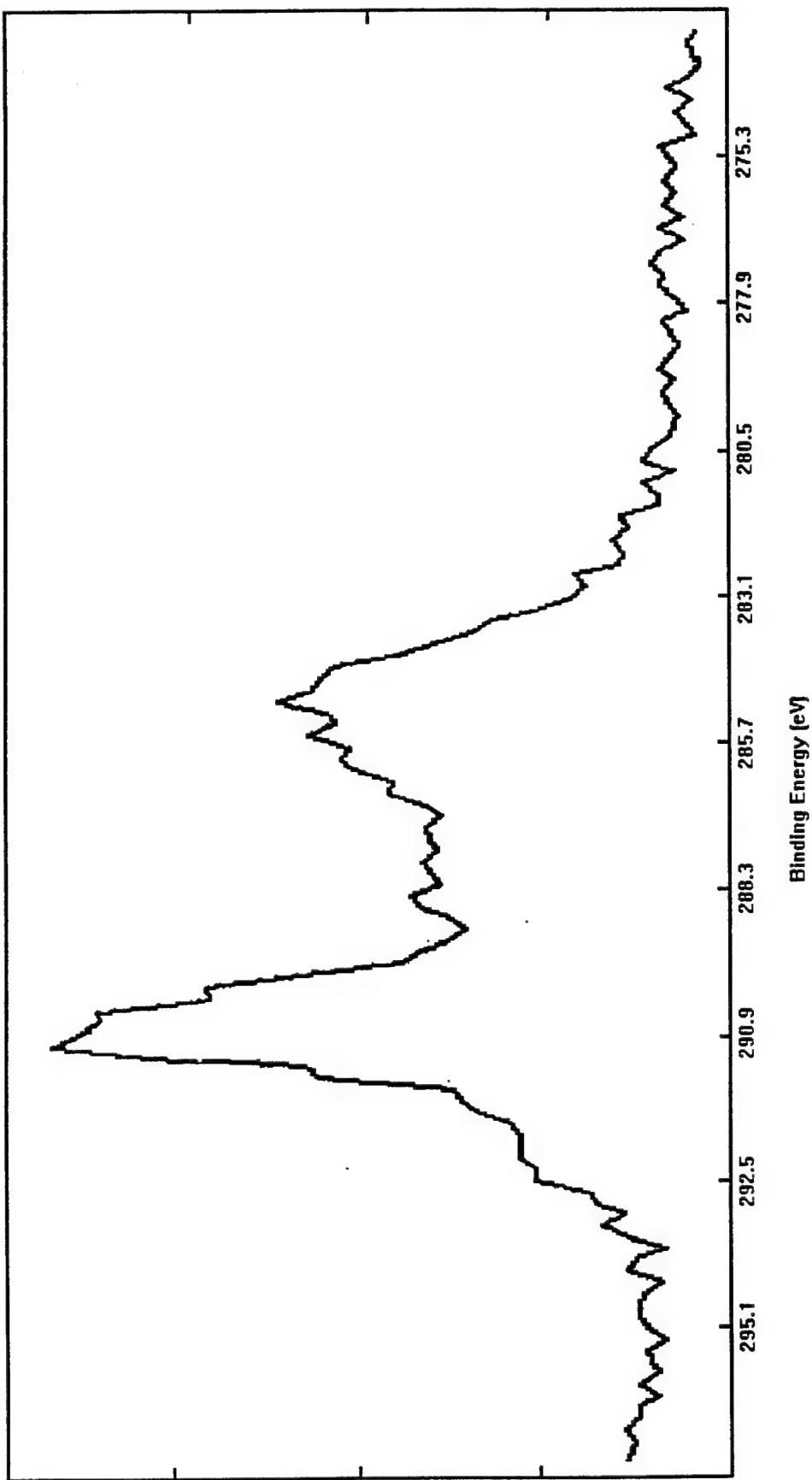


Fig. 16



Atomic Percentages of Fluorine for Polyamides

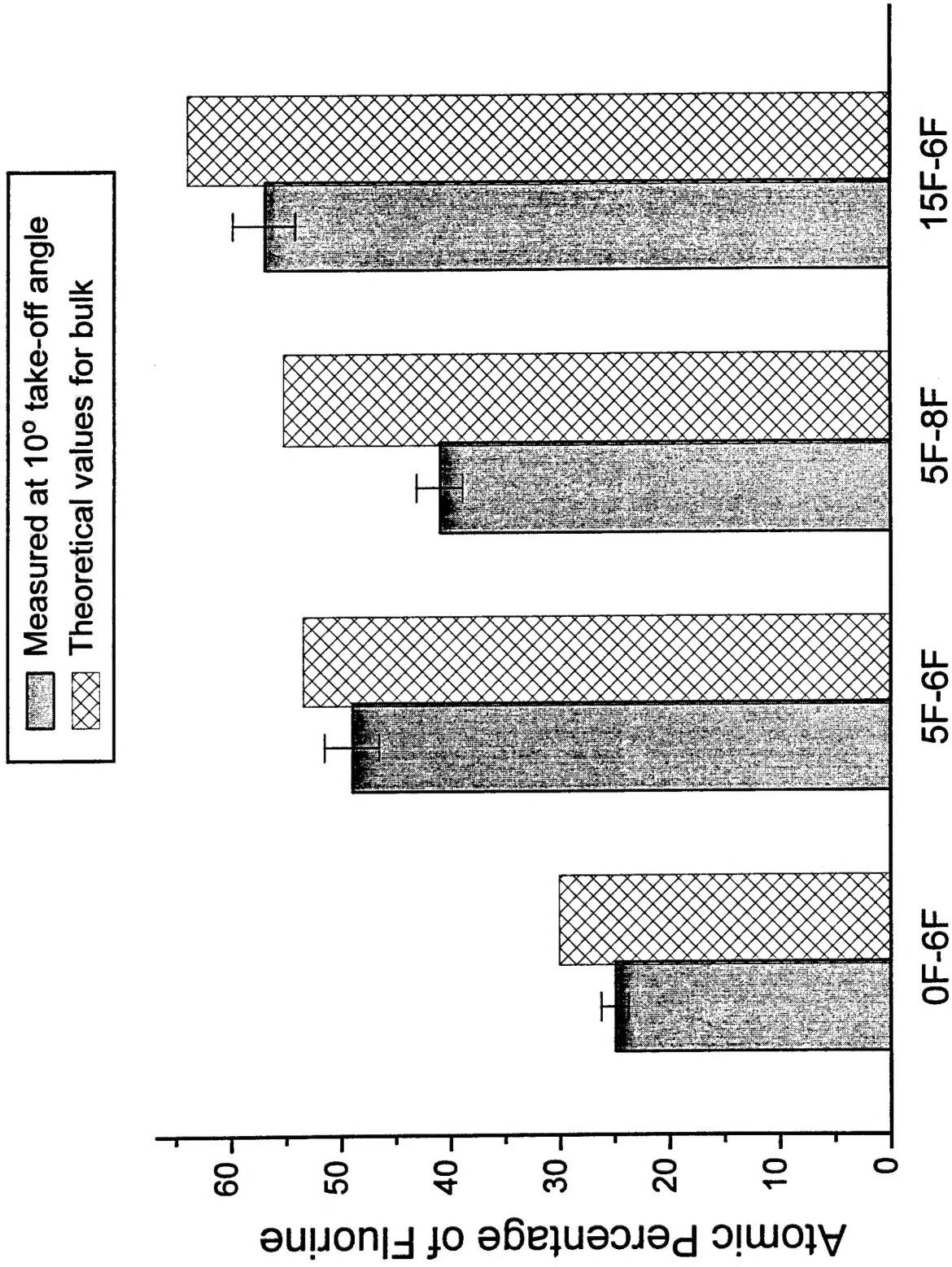


Fig. 2

Atomic Percentages of Fluorine for Poly(amide urethane)s

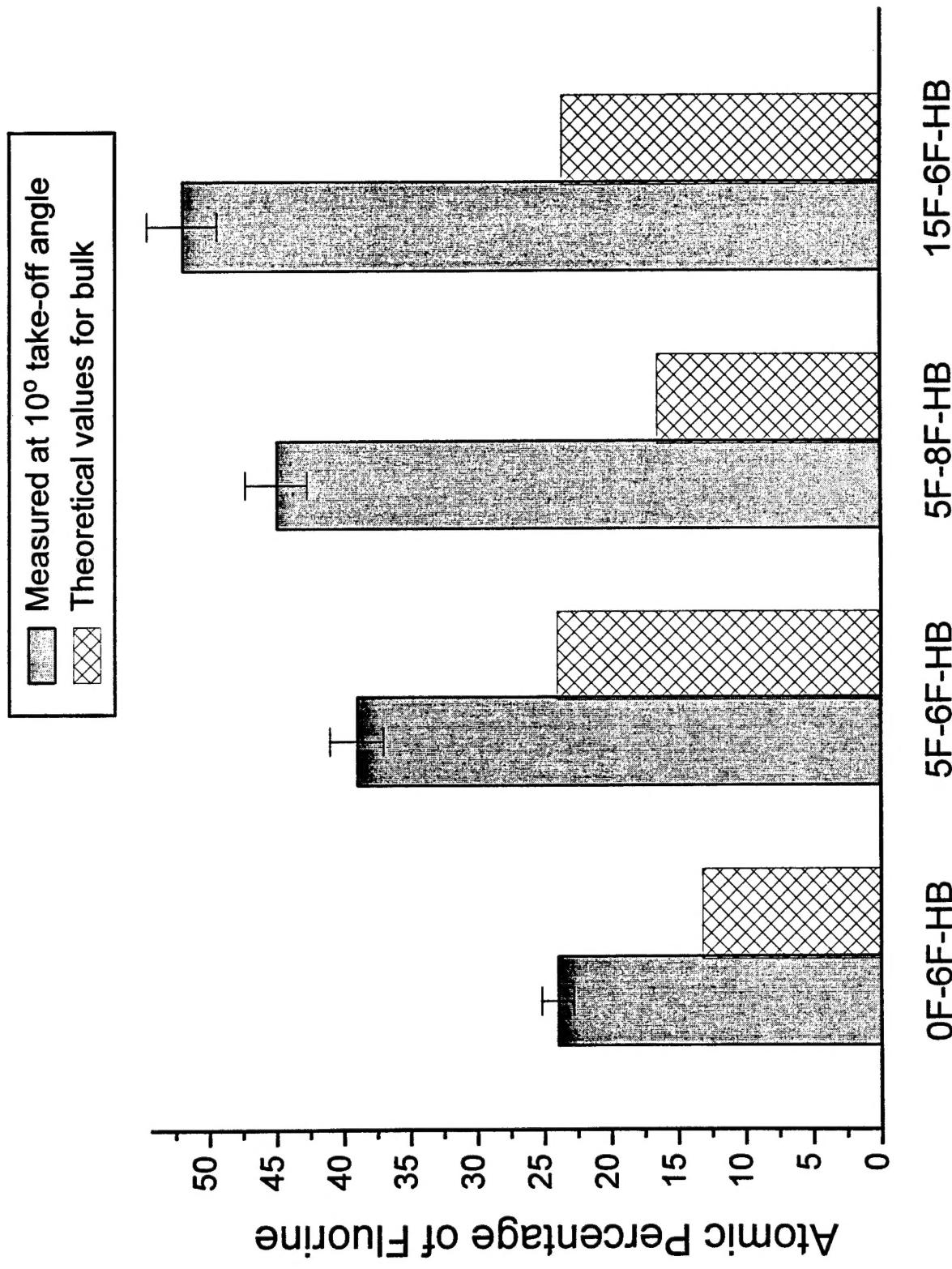


Fig. 3

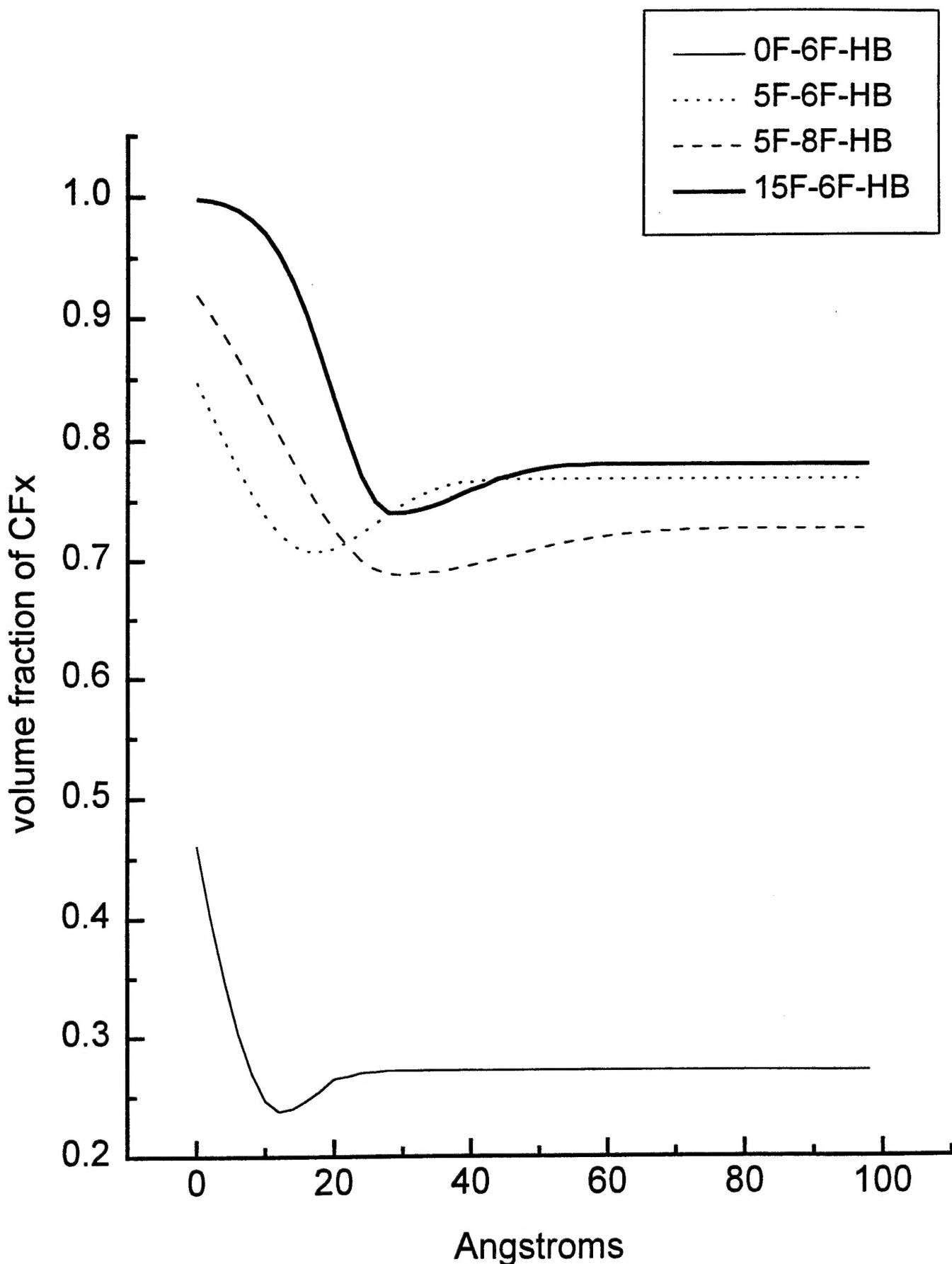


Fig. 4

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